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NEW NON-HALOGENATED FIRE RETARDANT FOR COMMODITY AND ENGINEERING POLYMERS

This invention is directed to the use of zirconia, ZrO_2, or ZrO_2 combined with a boron compound, such as boric acid, H_3BO_3, or ammonium pentaborate, $NH_4B_5O_8$, as fire retardants, for example in polymers such as commodity and engineering polymers, to fire retardant materials containing such a fire retardant and to methods for making materials fire retardant by use of such fire retardant agent.

Background of the Invention

Current fire retardants have a number of problems depending on the system. Halogen based fire retardants produce toxic and corrosive combustion products. Halogen as well as phosphorus based fire retardants increase the amount of carbon monoxide and smoke during combustion. Hydrates, which decompose by an endothermic process to produce water, must be used at such high loadings (e.g., 40-70% wt.) that the physical properties of the base polymer are excessively compromised. Further, most current fire retardants normally lose most or all of their effect at very high heat fluxes. Marchall, A., Delobel, R., Le Bras, M., Leroy, J., and Price, D., *Polymer Degradation and Stability*, 44, 263-272 (1994).

New fire retardants are needed that do not have these shortcomings. This is especially important for U.S. companies trying to sell products in Europe. In Europe a negative public opinion exists toward halogen-based fire retardants. This combined with a new environmental law, the "eco-labelling" law, requiring a label on all products that describes what materials were used in the product is forcing companies to look for new, environmentally acceptable fire retardants for their FR (fire retardant) polymer products.

Prior art on the use of zirconia as a fire or flame retardant is limited to its optional use in combination with hexavalent oxygenated sulfur compounds, see U.S. Patent No. 5,424,344 to Lewin. The use of zirconia as a filler or pigment in polymers is also known in the art; see, e.g., GB 2,255,345 and U.S. Patent No. 4,965,296.

Summary of the Invention

An object of the invention is to provide fire retardant agents which avoid the problems of the prior art.

Upon further study of the specification and appended claims, further objects and advantages of this invention will become apparent to those skilled in the art.

Objects of the invention are achieved by the discovery that zirconia or zirconia combined with boron-containing compounds provide very effective fire retardant agents.

For example, the use of zirconia or zirconia-borate combinations as additives in organic polymers reduces polymer flammability without any of the problems associated with the prior art. A special advantage of this system is that the effectiveness of this flame retardant (FR) is maintained even at very high heat fluxes (e.g., up to about 70 kW/m^2 or higher).

As an embodiment of the invention, it has been discovered that zirconia, alone, provides a useful and advantageous fire retardant effect. The form of the zirconia (ZrO_2) is not limited and any form may be used. Particularly, this is the case since it is theorized that, when heated to temperatures at which fire retardant activity is needed and exhibited, zirconia will modify to the form in which the fire retardant effect is provided. It is preferred, for example, to use a powder form of zirconia such that it can be readily dispersed in the material in which it is incorporated. Furthermore, the zirconia can be provided as a zirconia precursor which is converted to zirconia upon heating under the conditions where flame retardant activity is required. Examples of such zirconia precursors include solutions or gels of zirconium-containing compounds such as organometallic zirconium compounds. Particular examples include, but are not limited to, zirconium alkoxides or acetates.

Although zirconia may be used alone, it is preferred that the zirconia be used together with a boron-containing compound to exhibit the desired fire retardant activity. Preferred boron-containing compounds are boric acids or borate compounds, particularly borate salts. The salts may be obtained by reacting boric acids with bases such as ammonium compounds or potassium carbonate. Ammonium borate salts are preferred since they generate ammonia which aids flame retardant activity. Examples of particular boron-containing compounds useful for the invention include, for example, boric acid (H_3BO_3) and ammonium pentaborate ($NH_4B_5O_8$).

The relative amounts of zirconia and boron-containing compound are preferably such that the weight percent of zirconia based on the total weight of zirconia and boron-containing compound is from 100% (no boron-containing compound) to 5%, more preferably 75% to 25% and particularly preferably about 50%.

The flame retardants according to the invention are particularly useful in that they exhibit flame retardant activity even at high heat flux. While many flame retardant materials can meet prevailing standards as to heat flux operating limits, these standards are often too low to reflect real life flame retardant needs. The flame retardants according to the invention are advantageous in that they provide useful flame retardant activity at heat flux of, for example, about 70 kW/m^2 or higher, particularly up to about 120 kW/m^2 or at least up to about 100 kW/m^2.

The following Table 1 shows the advantageous properties of use of a flame retardant according to the invention in several types of polymers, i.e. PE (polyethylene), polypropylene, PT-30™ (a phenolic triazine), and polyetherimide. The additive is a flame retardant of ZrO_2 and ammonium pentaborate in a 1:1 weight ratio. The percentage of additive is based on the weight of polymer.

Table 1

Polymer Sample (heat flux kW/m²)	Char Yield (%)	Peak HRR (Δ%) (kW/m²)	Mean HRR (Δ%) (kW/m²)	Mean Heat of Combustion (MJ/kg)	Total Heat Released (MJ/m²)	Smoke: Ext. Area at 60s (m²/kg)	Mean CO yield (kg/kg)
PE (35 kW/m²)	0	1,820	1,110	40	240	443	0.03
PE 10% additives (35 kW/m²)	~1	829 (54%)	579 (48%)	37	246	641	0.03
Polypropylene (50 kW/m²)	0	2,074	920	40	262	650	0.04
Polypropylene 10% additives (50 kW/m²)	~3	800 (61%)	544 (41%)	37	206	665	0.04
PT-30™ (70 kW/m²)	58	973	336	15	59	430	0.03
PT-30™ 20% additives (70 kW/m²)	72	186 (81%)	96 (71%)	12	49	470	0.02
Polyetherimide (70 kW/m²)	52	173	88	12	45	465	0.07
Polyetherimide 20% additives (70 kW/m²)	70	114 (34%)	76	12	23	292	0.06

* The data are generated by use of a Cone calorimeter (see Babrauskas et al., *Fire Safety Journal*, 18, p. 255 (1992).

The data demonstrate that the fire retardant according to the invention can reduce the peak heat release rate (Peak HRR) in a polymer subject to a 70 kW/m^2 heat flux by as much as 81%. In general, the fire retardants according to the invention can reduce peak HRR in polymers by from 55-90%, even at a heat flux of 70 kW/m^2 or higher. This property makes them of particularly useful application in polymers to impart flame retardance thereto.

Figure 1 also shows Cone calorimeter data for polypropylene (PP) polymers containing a flame retardant of ZrO_2 and ammonium pentaborate in a 1:1 weight ratio according to the invention. The graph shows the reduction in R.H.R (same as HRR), at 50 and 70 kW/m^2 heat flux over time when 10% by weight of the additive is added to polypropylene. In each case the peak HRR is reduced to about half the peak HRR without the additive.

Although not intending to be bound by this theory, it is hypothesized that the zirconia and zirconia/boron-containing compound combination exhibit an intumescent activity which makes them useful flame retardants. Hence, particularly when used in connection with polymers, the flame retardants according to the invention produce a thermal shield which is able to protect the polymer material from external heat flux and also inhibit the escape of volatile fuels and oxygen diffusion which would otherwise feed the flames. See e.g. the Marchall et al. article cited above, which discusses intumescence. An observed phenomena of the invention herein which may relate to the intumescent effect is that the heating of, particularly, zirconia and a borate together results in a white foam-type of material referred to as "white char".

Although zirconia alone or zirconia with the boron-containing compound may be used solely as fire retardant it may also be useful to include other known fire retardant agents in addition to those of the invention. Such other useful agents include gas phase inhibitor flame retardants which are known in the art. Typical such agents are halogen compounds with or without antimony compounds, although, it is preferred for the reasons discussed above that halogen compounds not be included in the flame retardants. Also, useful are solid phase flame retardants, particularly, water-generating compounds such as inorganic hydroxide compounds, for example, aluminum trihydrate or magnesium hydroxide. Further, ammonia-generating compounds, such as, for example, melamine are useful in combination with the flame retardants of the invention. Other intumescent materials may be used in addition to those of the invention. These include, particularly, well known phosphorus-containing flame retardants.

It has been discovered that a particularly useful additive with the zirconia or zirconia and boron-containing compound flame retardants of the invention is inositol. This sugar-type compound provides an advantageous dual function of producing water and exhibiting a charring effect both of which aid in flame retardance. It is preferred to use inositol in this manner in an amount of 5 to 50% weight based on the total amount of flame retardant. For example, a composition of ZrO_2, a borate and inositol in a weight ratio of 1:1:2, respectively is useful as a flame retardant.

Although, as discussed above, known flame retardant agents can be used in combination with those of the invention, it is particularly preferred if the flame retardant is absent, completely or in any significant amount, of sulfur-containing compounds and/or toxic metal-containing compounds, such as zinc.

As mentioned above, the flame retardants of the invention are particularly useful for imparting flame retardant properties to polymers by incorporating them into the polymers, for example, by chemically bonding the agent into the polymer. The flame retardant can be used in any polymer in which flame retardant activity is required or desired. For example, the flame retardant can be used in commodity polymers, such as, for example, polyethylenes, polypropylenes, nylons, polystyrenes, thermoset polymers and inorganic polymers, and in engineering polymers. The flame retardant can provide even polymers considered to have low flammability with flame retardant activity. For application in polymers, the flame retardant, preferably in a dispersible form, may be mixed to suitable dispersion in the polymer during its preparation. Although any amount of the flame retardant may be used in the polymer, it is preferred to use from about 5-20% by weight of flame retardant in the polymer to obtain the flame retardant effect without an adverse effect on the physical properties of the polymer.

It is particularly advantageous to use the flame retardants in polymers which are to be used in carpeting, adhesives, wire or cable insulations, fabrics, furniture and other household, business or industrial products wherein flame retardance is desired.

The use of the flame retardants is, however, not limited to their application in polymers as described above. The flame retardants may be used as a coating or incorporated into a coating for coating a material, including but not limited to polymers, to provide a flame retardant shield on the material. Further, the flame retardants can be incorporated into materials other than polymers to provide a flame retardant activity therein.

Accordingly the invention is directed, in part, to the use of an agent comprising zirconia (ZrO_2) but excluding a sulfur-containing compound as a flame retardant. Further, the agent may also comprise a boron-containing compound, particularly wherein the boron-containing compound is a boric acid or borate salt. The invention is further directed to methods for making materials flame retardant by incorporating such an agent therein or coating the material with a coating containing such agent. The invention is also directed to materials which incorporate such agent or materials which are coated with a coating containing such agent to make them flame retardant.

The entire disclosure of all applications, patents and publications, cited above, are hereby incorporated by reference.

The preceding can be repeated with similar success by substituting the generically or specifically described reactants and/or operating conditions of this invention for those used therein.

From the foregoing description, one skilled in the art can easily ascertain the essential characteristics of this invention, and without departing from the spirit and scope thereof, can make various changes and modifications of the invention to adapt it to various usages and conditions.